

Reaction Products of Ozone: A Review

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The reaction products of ozone that form during the oxidation of compounds found in aqueous media are reviewed. Reaction products of ozone are well documented only for a limited number of substrates, and mechanistic information is quite rare. Decomposition of ozone during its reactions, sometimes induced by matrix impurities or by the by-products of the reactions, will generate highly reactive hydroxyl radicals. Thus, even reactions occurring at $\text{pH} < 7$ may have radical character. More complete destruction of organic substrates may be enhanced by using catalysts, such as ultraviolet radiation or hydrogen peroxide, to accelerate radical formation. However, complete mineralization is generally not practical economically, so partially oxidized by-products can be expected under typical treatment conditions. Ozone by-products tend to be oxygenated compounds that are usually, but not always, more biodegradable and less toxic than xenobiotic precursors. Of particular interest are hydroperoxidic by-products, which may have escaped detection because of their lability, and unsaturated aldehydes. Inorganic by-products tend to be in high oxidation states, which in some cases (e.g., some metallic elements) may lead to enhanced removal by flocculation and sedimentation. In other cases oxidation may lead to formation of reactive species such as hypobromous acid from bromide ion or permanganate from manganous ion. In general, more research is required before a valid assessment of the risks of ozone by-products can be made.

Introduction

Although the use of ozone for water treatment in the United States is not currently very widespread, use is increasing at such a rate that attention to ozone by-products must be given a higher priority than in the past. For example, the City of Los Angeles is constructing a very large ($26 \text{ m}^3/\text{sec}$) direct-filtration plant that will incorporate preozonation at approximately 1 mg/L .

There is no doubt that ozone used in water purification will produce chemical by-products. What is needed is an understanding of the nature of these by-products, their stability, and their potential health effects. At the present time, our knowledge in this area is quite limited, and from a public health perspective such information should be obtained before ozone use becomes widespread.

This paper will examine information on by-product formation from oxidation of some inorganic and organic substances in water. Ozonation will be the primary oxidation process considered, but because similar chemical intermediates are involved, other oxidation processes are very likely to yield similar by-products. Substrates of primary interest will be natural aquatic organics, sometimes referred to as humic substances, humic acids, or fulvic acids; volatile chlorinated hydrocarbons, which are so often observed in groundwaters; and miscellaneous other organics such as pesticides, which may

be important contaminants of concern for particular water utilities.

Aqueous Chemistry of Ozone

The chemistry of ozone in nonaqueous solvents has been the subject of research since the latter half of the nineteenth century. Bailey (1) has reviewed this subject in a two-volume treatise, covering also what was known until mid-1980 of aqueous ozone chemistry. However, much has occurred since that time, particularly in the area of the nature of ozone reactions at high pH values. Many of these advances in our knowledge are due to Hoigne and coworkers, whose elegant works have shown that at high pH values ozone acts not just by direct reaction of ozone (O_3) but by formation and reaction of the hydroxyl radical, one of the most reactive of the oxygen species (2). Hoigne has built on the works of Taube et al. (3), Hart et al. (4), Baxendale et al. (5), and others to construct a clear picture of the key oxygen-containing intermediates that are present when ozone decomposes.

Figure 1 is a diagram that shows the principal species present in the decomposition of ozone, a cyclic chain process (6). This chain may be initiated by a base such as hydroxide ion (4) as shown in Figure 1, or, as shown in Figure 2, by hydrogen peroxide added directly (7), or produced *in situ* by photolysis of ozone (3,8,9). The essential feature of the chain decomposition mechanism is the formation of the hydroxyl radical (OH), an extremely reactive species that can attack almost any organic substance. It is now clear that the hydroxyl radical may be formed during ozonation by one of several pro-

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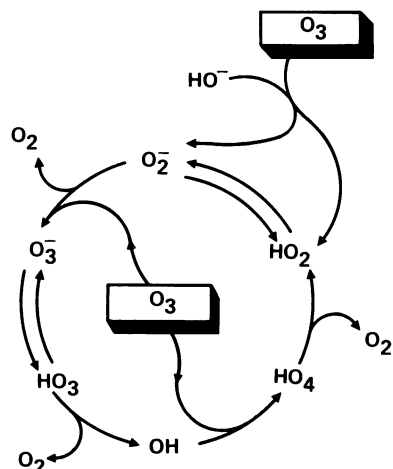


FIGURE 1. Cyclic chain mechanism for the decomposition of aqueous ozone initiated by hydroxyl ion. After Hoigne (6).

cesses as shown in Figures 1 and 2. Thus, reactions of organic compounds with ozone should be viewed not only in terms of the chemistry of the ozone molecule, as organic chemists have become accustomed, but also in terms of the chemistry of the hydroxyl radical.

Figure 3, following Hoigne (10), illustrates the two key pathways that are available for destructive oxidation of organics in water. Both pathways may result in the formation of hydrogen peroxide or formic acid, which can initiate chain decomposition of ozone, with the formation of hydroxyl radicals. Thus, even reactions that are carried out at pH < 7 may have a component of radical character, and the products from the two pathways shown in Figure 3 may be difficult to distinguish.

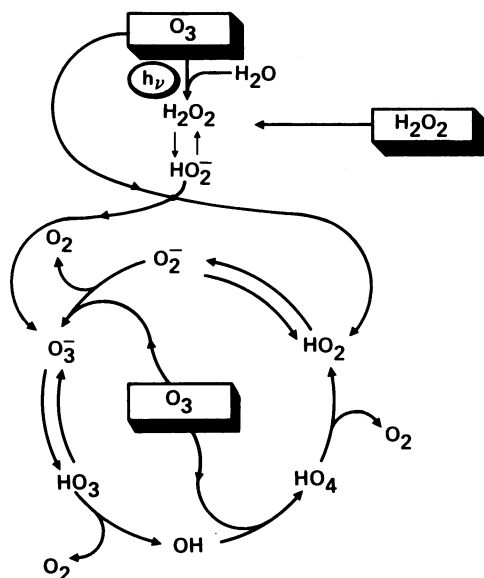


FIGURE 2. Cyclic chain mechanism for the decomposition of aqueous ozone initiated by UV radiation or addition of hydrogen peroxide.

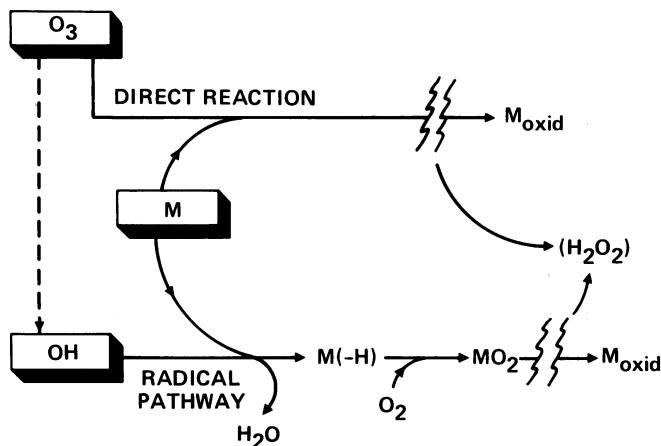


FIGURE 3. Reaction scheme for ozone showing direct reaction and hydroxyl radical reaction. After Hoigne (10).

As noted above, hydroxyl radicals are generally more reactive than ozone, less discriminating in the types of functional groups they will attack, and as a result, more subject to being trapped by a variety of matrix impurities. Bicarbonate ion, which traps hydroxyl radical very efficiently, is a common component of natural waters. Thus, waters that have high alkalinity values may not be favorable for efficient use of hydroxyl radicals (2,11).

Ozone itself is not always very reactive toward organic compounds. In general, compounds should have unsaturated linkages such as alkenes, acetylenes, aromatics, thiophosphates, etc. Aromatics should be activated to electrophilic substitution, i.e., phenols, aromatic ethers, etc. Amines are also susceptible to attack by ozone (12,13). Hydroxyl radicals will react with all these substances plus so-called refractory aliphatics such as alcohols, short-chain acids, etc. (14).

Some examples taken from the literature will serve to illustrate the types of by-products produced by ozonation in water. Unfortunately, few of these studies have been very definitive in terms of reaction pathways, and in many cases the products have not been carefully characterized.

Oxidation of Chlorinated Organics

The oxidation of chlorinated organics is of interest because of the number of cases of groundwater contamination by volatile chlorinated compounds; the widespread occurrence of chlorinated solvents, pesticides and industrial chemicals in streams and rivers; and the need to develop treatment schemes that will destroy these compounds not transfer them to another phase.

Chlorinated organic compounds such as chloroform and the chlorobenzenes do not react with ozone very rapidly under neutral or acidic conditions (12,15). Olefinic halides are more reactive, however, and compounds such as vinyl chloride and trichloroethylene will

submit to ozonation. No products studies have been reported, however. Glaze and co-workers studied the oxidation of chloroform, tetrachloroethylene, and 2,2', 4,4', 6,6'-hexachlorobiphenyl (HCB) by ozone with ultraviolet (UV) radiation (16). The results are summarized in Table 1. Also included are the results reported by Yokayama and co-workers on the ozonation of 2,2'-dichlorobiphenyl (17) and Legube et al. on 2-methyl-4-chlorophenoxyacetic acid (18).

The observation (16) of trichloroacetic acid in the reaction mixture after photolytic ozonation of tetrachloroethylene (PCE) is surprising. Perhaps it is formed by 1,2-shift of a chloride radical within the adduct of PCE and the hydroxyl radical (I) to form the radical (II) (Fig. 4), since similar isomerization reactions have been observed in the radiolysis of alkyl halides (19). In fact, a commercial process for trichloroacetic acid is built on the radiolysis of PCE (20). Although Koster and Asmus did not report isomerizations of this type in a study of the aqueous radiolysis of chloroethylenes, including PCE, they did not use methods to determine trace organic by-products (21). On the basis of spectrographic data collected during pulse radiolysis, Koster and Asmus postulated the elimination of hydrochloric acid (HCl) from I to yield the carbonyl radical (III). If the radical II is formed, it would yield IV by a similar process; IV would then yield trichloroacetic acid after capture of oxygen and hydrolysis.

Polychlorinated biphenyls yield ring-cleavage reaction products that may be of some health significance since they retain halogen atoms (Table 2). One ring is virtually completely oxidized before the second ring halogen is attacked. Thus, after incomplete oxidation, which is to be expected under practical water treatment

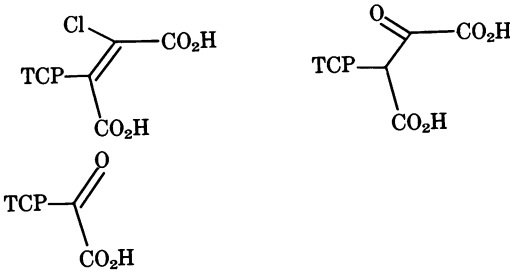
conditions, these types of by-products are very likely to remain if their precursors were initially present. Once the ring is ruptured, however, dechlorination reactions proceed rapidly.

A reaction scheme has been proposed to account for the products observed in the oxidation of HCB shown in Table 2 (16). The initial steps, as in the case of phenol and other aromatic compounds, is probably ring hydroxylation, which activates the ring to direct attack by ozone. In the case of unactivated aromatics such as halides, hydroxylation may require hydroxyl radicals, which explains the rather slow rate of the process when no radicals are present, i.e., when ozone is acting directly. With ozone/UV or high pH conditions, the rate is substantially accelerated.

Oxidation of Miscellaneous Aromatic Compounds

Dore and co-workers (22) at Poitiers and Gilbert at Karlsruhe have been most prolific in this area. Their works have shown, as noted above, that ozonation of aromatics is slow except when activating groups such as hydroxyl, amino, etc., are present. Few studies have looked carefully at the by-products from ozonation reactions, and no detailed mechanistic studies have been published. A few recent results are summarized in Table 2 primarily to reemphasize that the major products are due to ring cleavage. In Table 2, the term RFP refers to ring fragmentation products, i.e., the 4-, 3-, and 2-carbon acids, aldehydes, and carboxyaldehydes that are always produced when aromatic compounds are oxidatively cleaved with ozone (1).

Table 1. Oxidation by-products of halogenated organics.

Compound	Products identified	Reference
Chloroform	CO ₂ , Cl	(16)
Tetrachloroethylene	Cl ⁻ , CCl ₃ COOH	(16)
Hexachlorobiphenyl ^a	 TCP-CO ₂ H TCP-H TCP-OH	(32,16)
4,4'-Dichlorobiphenyl ^b	CP-CO ₂ H	(17)
2-Methyl-4-chlorophenoxyacetic acid	unchlorinated ring fragmentation products	(18)

^a Hexachlorobiphenyl is the 2,2',4,4',6,6' isomer; TCP refers to the 2,4,6-trichlorophenyl radical.

^b CP refers to 4-chlorophenyl radical.

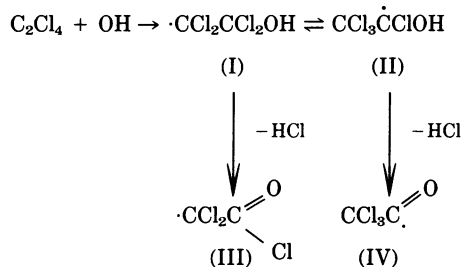


FIGURE 4. Possible scheme for the formation of trichloroacetic acid during the photolytic ozonation of tetrachloroethylene (16).

Two additional aspects of aromatic ozonation processes are of interest. First, there is the question of whether ring hydroxylation occurs through addition of ozone (either bipolar or pure electrophilic attack) or through the intermediacy of hydroxyl radicals. Second, in a more practical vein, there is the question of whether the peroxidic ozonolysis products are stable enough to survive in water distribution systems. In general, hydroxyhydroperoxide intermediates are thought to form whenever ozone cleaves a carbon-carbon multiple bond.

Some of these peroxidic compounds are stable enough to be isolated from water/acetone or water/methanol solvents (1), so they may be stable enough to remain in dilute solution in water for hours or even days. However, there is no evidence that this occurs and it might be that the inorganic species in natural waters catalyze their decomposition more readily than one observes in laboratory water. It is interesting to note, however, that Legube et al. (15) have measured rather substantial amounts of hydrogen peroxide when styrene and other aromatics were ozonized. The analytical method they use for peroxide is one that may give positive results if organic peroxides are present (23); therefore, the question remains open.

Ozone By-Products of Aquatic Organics

Several groups of workers have attempted to identify ozonation by-products of isolated samples of humic acid and fulvic acid, and some have oxidized the entire pot-

Table 2. Ozonation products of selected aromatic compounds.

Compound	By-products ^a	Reference
Styrene	Benzaldehyde, benzoic acid, H ₂ O ₂ , RFP	(15)
Naphthalene	Phthalic acid, <i>o</i> -carboxybenzaldehyde, H ₂ O ₂ , RFP	(15)
Phenol	Pyrocatechol, hydroquinone, <i>p</i> -quinone, RFP	(15)
Aniline	RFP	(18)
Phenoxyacetic acid	RFP	(18)
<i>p</i> -Cresol	RFP	(18)
Glyoxal	Glyoxylic acid, oxalic acid	(22)
Glyoxylic acid	Oxalic acid	(22)

^a RFP refers to various ring fragmentation products (see text).

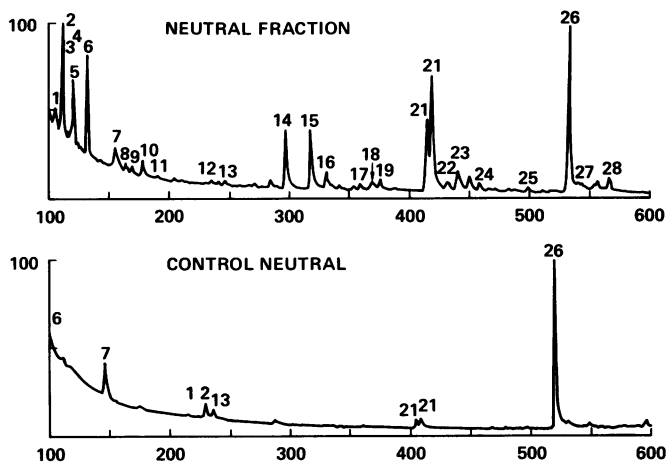


FIGURE 5. Reconstructed total ion chromatogram of XAD 4/8 extracts of surface water source before (lower curve) and after ozone treatment at 3.5 times TOC concentration (w/w basis). Fraction isolated with water at pH 12.

pourri of organics in natural waters (24–27). Some small molecules are produced during oxidation and it is these which have received the most attention, mainly because they are more tractable. Figures 5 and 6, not previously published in the open literature (28), are reconstructed gas chromatography/mass spectrometry (GC/MS) profiles for extracts obtained from a surface water source before (lower traces) and after ozonation (upper traces). The extracts were obtained by accumulation of the organics on a mixed bed of XAD-4 and XAD-8 and elution with diethyl ether (28). The acid fraction was derivatized with diazomethane before chromatography. Table 3 is a compilation of the compounds identified from their EI mass spectra. However, in most cases the identities were established only at confidence level two (29).

Lawrence and co-workers have ozonated fulvic acid isolated from soil and from a surface source containing

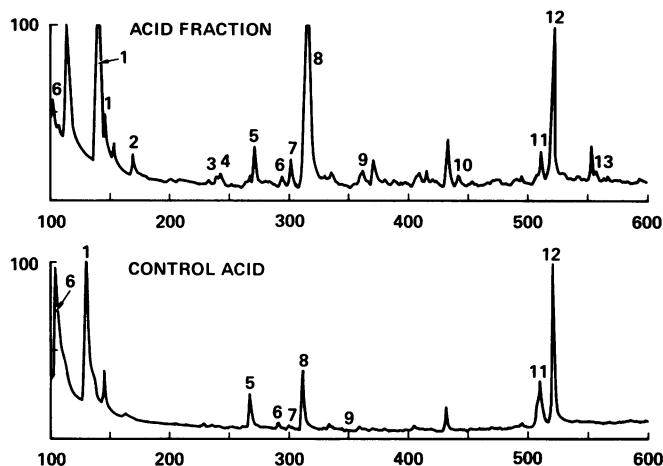


FIGURE 6. Same as Figure 5; acid fraction isolated after water adjusted to pH 2.

Table 3. Ozone by-products from a surface water source (28).

Neutral fraction ^b		Acid fraction ^c	
Code	Compound	Code	Compound
1	Methylcyclohexane	1	4-Oxo-2-butenic acid
2	2-Methyl-3-pentanone	2	2-Ethylpropenoic acid
3	3,4-Dimethyltetrahydrofuran	3	4-Oxopentanoic acid
5	Toluene	4	5-Methyl-3-oxohexanoic acid
6	4-Heptanone	5	Succinic acid
8	4-Heptanone	6	2-Methylbutandioic-1,4-acid
10	<i>o</i> -Xylene	8	Benzoic acid
14	Acetophenone	9	4-Methoxy-6-methyl-1,2-pyrone
15	Methyl benzoate	10	3,5-Dimethylbenzoic acid
16	1-Methoxyethylbenzene	11	Phthalic acid
17	2-(Methylphenyl)-acetaldehyde	12	Hexamethylbenzene (internal standard)
18	Ethylbenzaldehyde	13	Nonanedioic-1,9 acid
19	Naphthalene		
21	1-Valeryl-pyrrolidine		
22	4-Phenyl-2-butanone		
26	Hexamethylbenzene (internal standard)		

^a Ozone/TOC = 2.5; XAD-4/8 extract at pH 10 and 2; 5 L of water to 0.5 mL ether; internal standard added at 100 µg/mL.

^b Code numbers refer to Figure 5.

^c Acids determined as methyl esters after diazomethane conversion; code numbers refer to Figure 6.

high levels of fulvic acid (27). The water after treatment was sequentially extracted with petroleum ether, then ethyl acetate, and then methylated with dimethyl sulfate. Solvent extracts were evaporated to dryness then redissolved and methylated. As expected, this procedure focused on acidic compounds. A variety of organic acids were detected, including phthalates and fatty acids, the former presumably bound to the humic polymers as described by Ogner and Schnitzer (30). Several neutral compounds of interest were identified, including toluene and methylcyclohexane (see also Table 3) and four ketones (e.g., 2,6-dimethyl-2,5-heptadiene-4-one). The compounds were identified by comparison of mass spectra with library spectra and by manual interpretation (level one or two) (29).

Little has been learned from these studies relevant to the questions addressed in this symposium, since most of the compounds observed are expected to have no deleterious health effects. Most of the compounds found after ozonation of natural waters resemble those organics one can isolate from natural waters without treatment. This is reasonable in view of the fact that most natural organics have been subjected to environmental oxidation processes, in some cases for years. Some of these processes have similar chemical intermediates to those produced in ozonation processes (31), so it is no surprise that their products are similar. The possible exceptions to this generalization are certain aldehydes, such as compound 17, neutral fraction, Table 1; and as yet undetected hydroperoxides.

Overall, the principal effect of oxidation of the large humic molecules is probably not to destroy the polymer

structure (32) but to oxidize part of its functional groups. These changes, which are much like those which occur under natural conditions, will be difficult to detect spectroscopically. After years of searching, the precise structure of humic and fulvic acids is still not known, so it is not surprising that the effects of ozonation have also escaped elucidation. Much more research must be conducted before the by-products from the ozonation of natural organics will be understood.

Formation of Aldehydes by Ozonation

Several aldehydes have been observed as by-products of ozonation reactions, both of natural waters and of model compounds. Schalekamp reported the formation of straight chain aldehydes from the ozonation of Lake Zurich water (33). Sievers et al. (26) reported the formation of C₆–C₉ alkanals resulting from the ozonation of a domestic wastewater and attributed them to cleavage of unsaturated fatty acids. Two aldehydes are listed in Table 3, along with several carboxylic acids, which probably have aldehydic precursors. Aldehydes are also produced by cleavage of xenobiotic aromatic compounds as illustrated in Tables 1 and 2.

Some aldehydes are known to be severe hepatotoxins and have been identified as principal products of lipid peroxidation induced by agents such as carbon tetrachloride (34). Unsaturated aldehydes, i.e., enals, are particularly reactive with some biological molecules and have been shown to block both protein and DNA synthesis, among several other effects (35,36). In general, aldehydes are quite absorbable and diffusible and can have effects distant from the site of generation or administration. Recently, Segall and co-workers have shown that the enal *trans*-4-hydroxy-2-hexenal is formed by metabolism of macrocyclic pyrrolizidine alkaloids in the liver (36). Hence, lipids are not the only precursors of interest.

The foregoing does not prove that aldehydes associated with ozonation of natural waters will have any adverse effect on populations that consume these waters. What it does suggest is that further studies are required to determine the nature of ozone by-products, and that special attention should be given to the search for aldehydes, and in particular enals, and if the latter are found, to their precursors.

Ozone By-Products of Inorganic Species

Inorganic species will also be affected by ozone treatment of water. Some detrimental as well as beneficial side effects may result from these reactions. For example, it is now well known that ozone oxidizes bromide ion to hypobromous acid and then to bromate (37, 38). Under the proper conditions this reaction may yield brominated trihalomethanes and other organic by-products even in the absence of a chlorination step (39).

Ozone can also oxidize hypochlorite to chlorate and monochloramine to nitrate ion (40), which complicates the use of ozone with these substances during water treatment.

Conclusions

This paper elucidates several important concepts regarding ozone by-product information during water treatment.

Ozonation reactions may involve reactions of the ozone molecule or radical species, primarily OH, depending on the pH of the solution and the level of active chain initiators such as hydrogen peroxide, formate and ultraviolet radiation. Even at near-neutral pH, the reactions may involve radical character because peroxide is often a by-product of the ozonolysis process. The types and distribution of by-products will therefore depend on the nature of the water impurities.

In its reactions with natural organics, ozone (or its radicals) not only cleaves small molecules from the polymer chains, it also frees neutral molecules such as pesticides that may be complexed to the humic material.

Ozone can produce as well as destroy trihalomethane precursors; the precise level of the residual being dependent on reaction variables and water quality.

Ozone by-products are generally more polar and more biodegradable than their precursors, but there is less information available on toxicities of by-products. Of particular interest are some aldehydes, particularly enals, and compounds that may not survive some analytical separations, such as hydroperoxides.

Many types of organic compounds, such as chlorinated aromatics, chlorinated alkanes, unsubstituted alkanes, and monocyclic aromatics, are not amenable to destruction with ozone only. However, these types of compounds are subject to attack by radical producing systems such as ozone/UV, ozone at high pH values, etc.

Ozone will oxidize bromide ion to hypobromous acid, which may under certain conditions react with natural organics to produce brominated organics (such as bromoform) even in the absence of chlorine.

Finally, few detailed studies of aqueous ozone reaction mechanisms and by-products have been reported.

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